

CZOCHELSKI CRYSTAL GROWTH: MODELING STUDY

CHEMICAL REACTION ENGINEERING LABORATORY
DEPARTMENT OF CHEMICAL ENGINEERING
WASHINGTON UNIVERSITY
ST. LOUIS, MO

M. P. Dudukovic, P. A. Ramachandran, R. K. Srivastava,
and D. Dorsey

Summary of Accomplishments: Modeling the Cz Growth of Silicon

Modeling Approach

During the past eighteen months the CREL group at Washington University has established itself as a leader in mathematical modeling of CZ growth of silicon. The unique approach of this modeling group was to relate in a quantitative manner, using models based on first principles, crystal quality to operating conditions and geometric variables. Superior quality Si crystals need to be of uniform diameter, of high, axially and radially uniform, resistivity and defect free. The resistivity profiles can readily be related to imbedded dopant and impurity concentrations, while the dislocations are a strong function of the interface shape and residual stresses in the crystal. In turn the dopant distributions, interface shape and diameter are governed by the heat balance at the interface. Thus, it can be concluded that crystal quality can directly be related, in a quantitative way, to the hydrodynamics, mass and heat transfer in the melt and to heat transfer in and from the crystal. These phenomena are dependent on: geometric variables which are fixed for a given puller (e.g., crucible and enclosure shape, heater shape, etc.), process variables which are governed by the selected operating schedule (e.g., melt depth, height of exposed crucible wall, etc.), manipulated variables which could be used for control (e.g., heater power,

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crystal and crucible rotation speed, crystal pulling rate, heater position, gas flow rate, etc.). The variables to be controlled are crystal diameter and interface shape since they directly affect dopant distribution and residual stresses.

The systematic modular approach to this complex problem developed at CREL is shown schematically in Figure 1. The sketch of the puller is showing Figure 2. The finite element method is used for all calculations. The heat balance at the interface, which is the key element that governs crystal quality can be stated as:

$$(\text{Heat of Solidification}) \times (\text{Rate of Solidification}) =$$

$$\begin{array}{l} (\text{Heat Loss into} \\ \text{Crystal from the} \\ \text{Interface}) \end{array} - \begin{array}{l} (\text{Heat Transfer from} \\ \text{Melt to the Inter-} \\ \text{face}) \end{array}$$

$$\begin{array}{ccccccc} \rho V_G \Delta H \cos \alpha & = & (-k_c \frac{\partial T}{\partial n}) & - & (-k_m \frac{\partial T}{\partial n}) & & (1) \\ \text{I} & = & \text{II} & - & \text{III} & & \end{array}$$

Here term II is given by the heat transfer model for the crystal while term III is determined by the hydrodynamic and heat transfer model for the melt. Clearly, terms II and III dictate the interface shape through angle α and achievable pulling rate V_G at the fixed diameter. Equation (1) allows the general problem to be approached in a modular, sequential fashion. The rigorous model for the heat transfer in the crystal can be solved first and coupled with an approximate model for the melt. Melt models can be gradually improved and incorporated into the overall model as shown in Figure 1.

The above approach has been used successfully by the CREL group in modeling CZ of silicon and it should be directly extrapolable to modeling of GaAs.

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Major Accomplishments

1. A rigorous model based on first principles was established to predict the heat transfer in the crystal and the interface shape [Ramachandran and Dudukovic, J. Crystal Growth 71 (1985): 399-408]. The model is the first to have considered properly both direct and reflected radiation in the crystal enclosure. The model established two dimensionless parameters: a dimensionless flux at the interface and a Biot number as the key factors in determining the interface shape. This is confirmed by experimental data. The effect of including reflected radiation on axial temperature profiles is shown in Figure 3. The effect is even more dramatic for interface shape.
2. A coupled problem for the puller was solved based on an approximate conductor dominated heat transfer in the melt [Srivastava, Ramachandran and Dudukovic, J. Crystal Growth 73 (1985); 487-504]. Both, the Laplace-Young equation for the melt meniscus shape and Gebhart's enclosure theory for radiation were used. This paper provides a detailed account for the effect of all variables on interface shape. It is shown that reflected radiation is important especially in the vicinity of the interface.
3. Radiation view factors for short crystals during necking and shoulder growth are reported for the first time [Srivastava, Ramachandran and Dudukovic, J. Crystal Growth (1986) in print]. These are essential in simulating properly the critical initial stages of growth.
4. The detailed model developed and described under item 2 was simplified. Useful simple relations were developed for growth rate and interface shape as shown in Figure 4. The various parameters A , B , b , C_1 , C_2 , C_3 can be correlated with operating conditions. The simple models can then be run on line. [Srivastava, Ramachandran and Dudukovic, J. Electrochem.

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Soc. Solid State Sci. Techn. 133 (1985): 1007-1015]. The success of the simple models in matching the predictions of the detail models for growth rate versus radius and for interface shape versus radius are shown in Figure 5 and 6, respectively.

5. A novel concept of improving the controllability of the diameter and achieving decoupled diameter and interface shape control is introduced and numerically demonstrated [Srivastava, Ramachandran and Dudukovic, J. Crystal Growth (1986) in print]. The concept relies on regulating the convecting cooling component of the crystal by using gas jets.

Variations of gas flow rate or gas pressure can also be used. Predicted increases in productivity with increased jet cooling are illustrated in Figure 7.

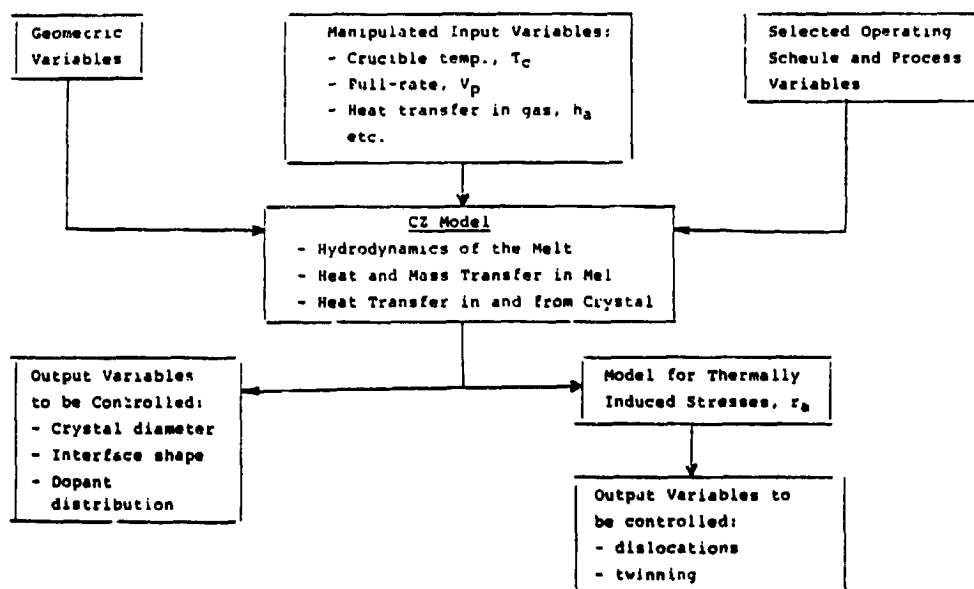
6. A preliminary steady state model for simulation of the hydrodynamics of the melt has been established [Dorsey, Ramachandran and Dudukovic, AIChE One Day Symp., St. Louis, April, 1985].

List of Publications Resulting from the Cz Modeling Work

at CREL at Washington University

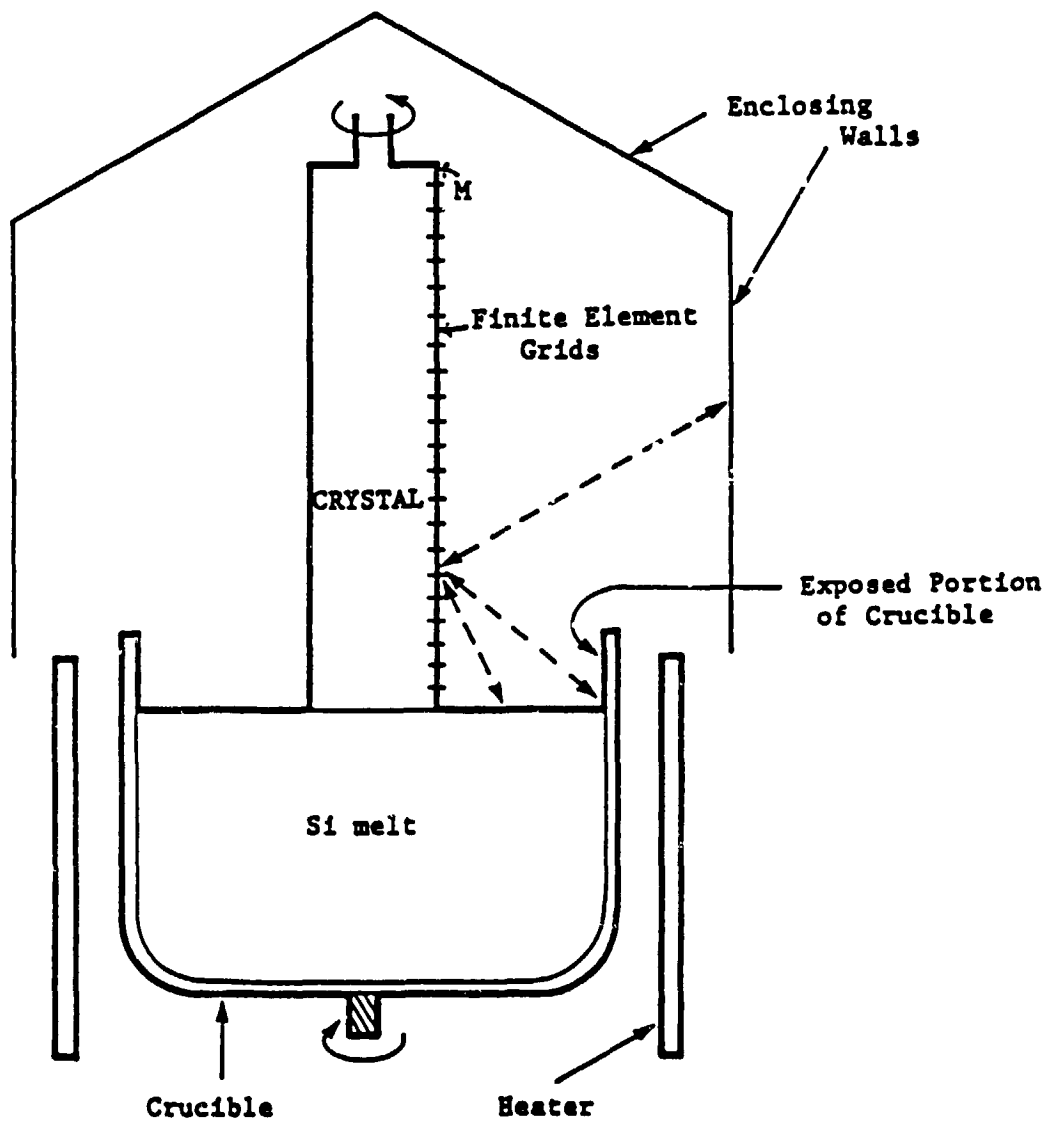
1. Ramachandran, P. A. and M. P. Duduković, "Simulation of Temperature Distribution in Crystals Grown by Czochralski Method", J. Crystal Growth 71 (1985): 399-408.
2. Srivastava, R. K., P. A. Ramachandran and M. P. Duduković, "Interface Shape in Czochralski Grown Crystals: Effect of Conduction and Radiation", J. Crystal Growth 73 (1985): 487-504.
3. Srivastava, R. K., P. A. Ramachandran and M. P. Duduković, "Radiation View Factors in Czochralski Crystal Growth Apparatus for Short Crystals", J. Crystal Growth (1986). In print.
4. Srivastava, R. K., P. A. Ramachandran and M. P. Duduković, "Czochralski Growth of Crystals: Simple Models for Growth Rate and Interface Shape", J. Electrochem. Soc.: Solid-State and Technology 133 (1985): 1009-1015.
5. Srivastava, R. K., P. A. Ramachandran and M. P. Duduković, "Simulation of Jet Cooling Effects on Czochralski Crystal Growth", J. Crystal Growth (1986). Accepted for publication.
6. Dorsey, D., P. A. Ramachandran and M. P. Duduković, "Numerical Simulation of the Hydrodynamics and Heat Transfer in Czochralski-Melts: Preliminary Results", AIChE One Day Symp., St. Louis, April 17, 1985.

Overall Schematic of Cz Modeling

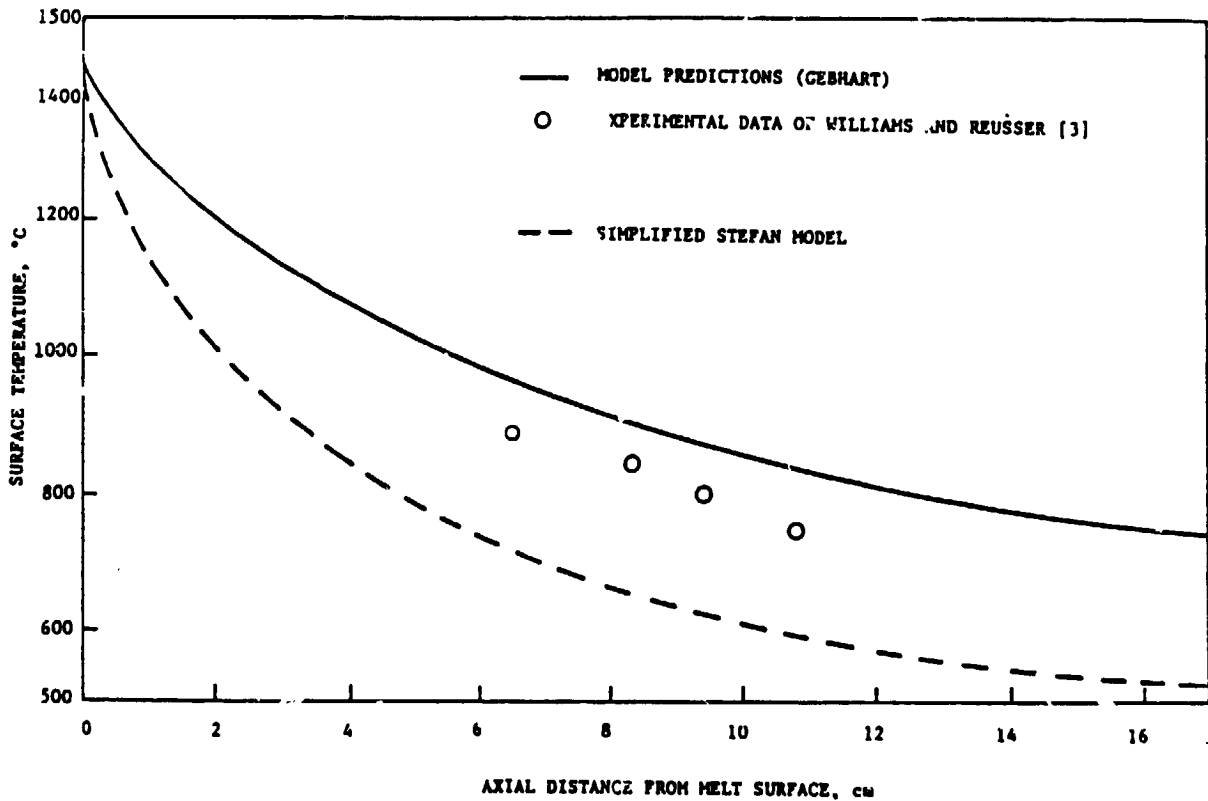


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Schematic of Cz Single Crystal Puller
(---Indicates Radiation Interaction Between Various Surfaces)



Predicted Crystal Surface Temperatures Based on Gebhart and Stefan Models and Experimental Results of Williams and Reuser
[from Ramachandran and Dudukovic,
J. Crystal Growth (1985): 399-408]



Simple Models for Growth Rate and Interface Shape

Developed from the predictions of the detailed heat transfer model

1. Growth rate

At const. T_c $V_g = \frac{A}{R} - B$; A and B are constants,
A depends on extent of jet cooling

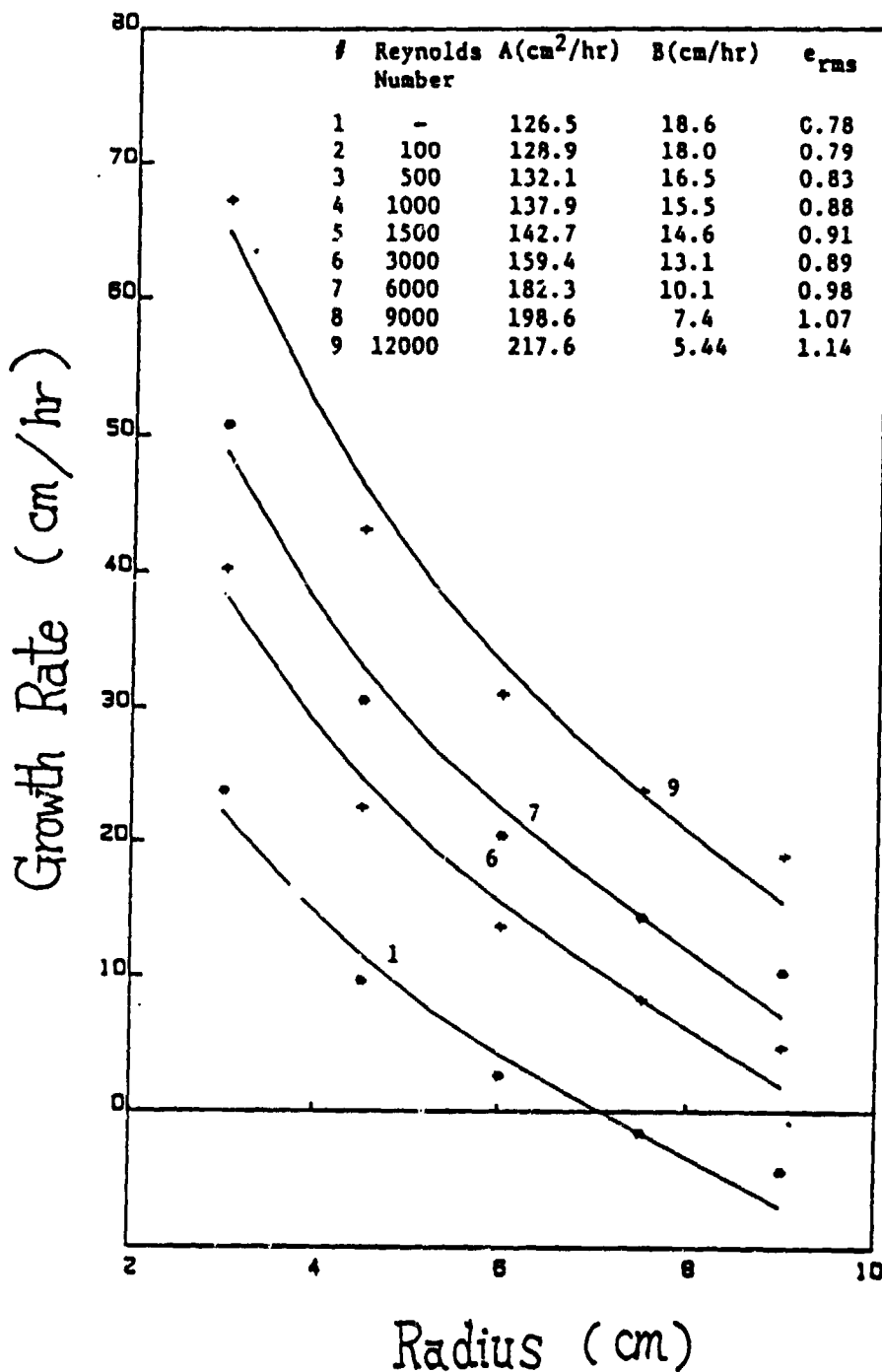
At const. R $V_g = V_{ms} - b\Delta T$; $\Delta T = T_c - T_m$

2. Interface shape

At const. T_c $\Delta R = GR - CR^2$

At const. R $\Delta R = \Delta R_0 - C_3 \Delta T$

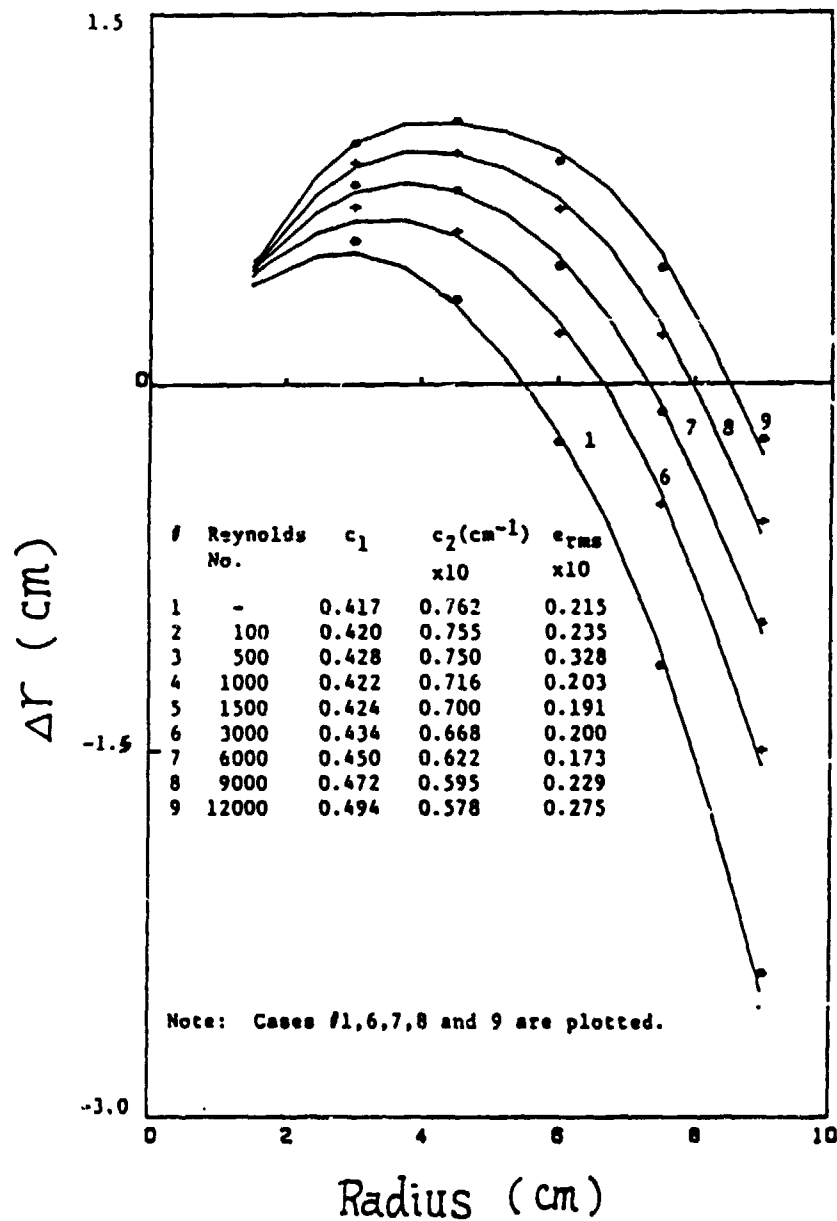
Comparison of Pulling Rate Versus Crystal Radius
(V Versus R)



———— Detailed Simulation
*** or +++ Approximate Equation

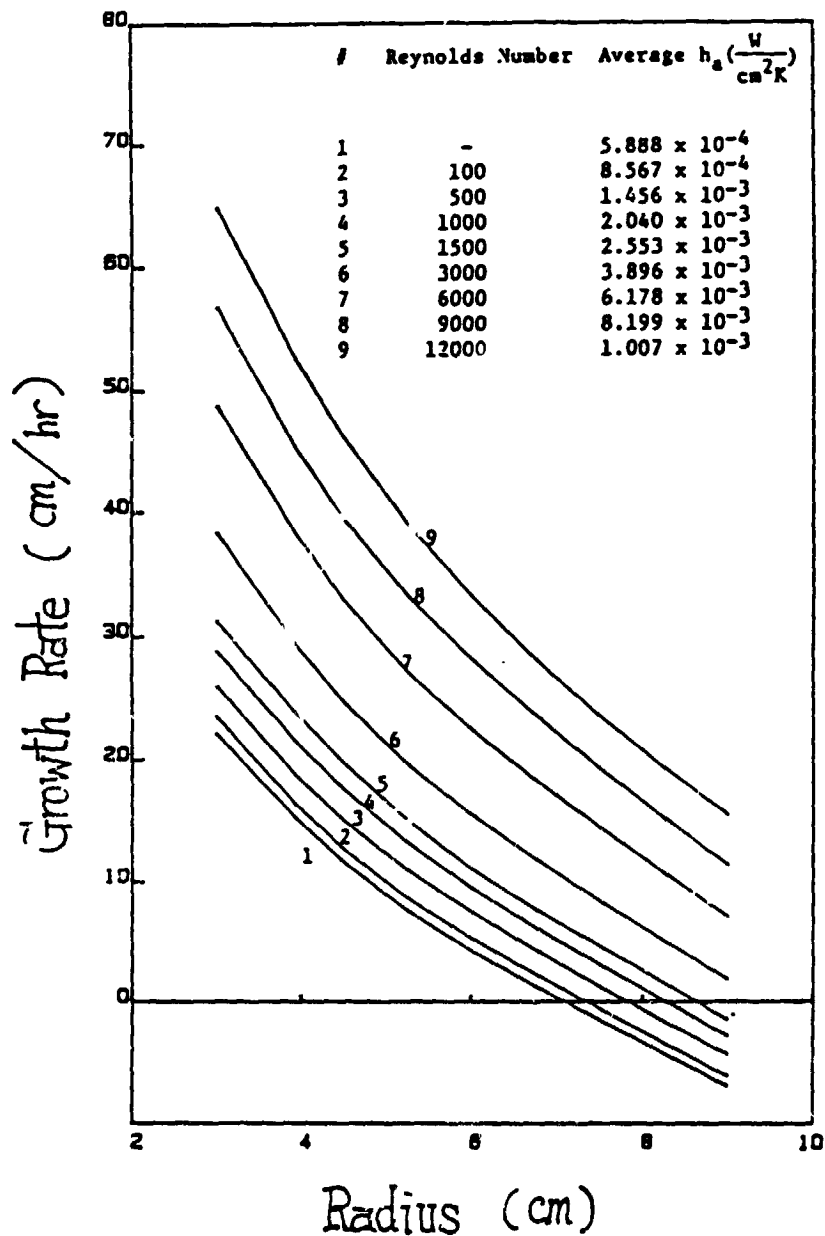


Variation of Interface Shape with Crystal Radius and Jet-Cooling



———— Detailed Model
 *** or ++ Approximate Equation

Variation of Growth Rate with Crystal Radius
at Different Levels of Jet-Cooling



HIGH-EFFICIENCY SOLAR CELLS

Paul Alexander, Chairman

Six presentations were made at this session on progress in high-efficiency solar cell research.

The presentation by the University of California, Los Angeles (UCLA), was on optimization methods for solar cell numerical models. A description was given on optimizing algorithms of solar cell models to simultaneously vary design variables such as impurity concentrations, front junction depth, back junction depth, and cell thickness to maximize predicted cell efficiency. The optimization methodology was demonstrated on Solar-Cell Analysis Program in One Dimension (SCAP1D), which is a computer program written by Purdue University, that relates a specific solar cell efficiency to a given set of input conditions such as cell thickness, impurity concentration, junction depth, etc. The UCLA optimization method, by iterating a set of input conditions from SCAP1D, provided a maximum solar cell efficiency related to ranges of input conditions that were derived from the SCAP1D inputs. UCLA presented curves of computer runs that demonstrated their optimization techniques.

The University of Pennsylvania described their work in identifying, developing, and analyzing techniques for measuring bulk recombination rates, and surface recombination velocities and rates in all regions of high-efficiency silicon solar cells. Professor M. Wolfe described their recent work of improving the accuracy of their previously developed DC measurement system by adding blocked interference filters. The system has been further automated by writing software that completely samples the unknown solar cell regions with data of numerous recombination velocity and lifetime pairs. The results can be displayed in three dimensions and the best fit can be found numerically using the simplex minimization algorithm. They also described a theoretical methodology to analyze and compare existing dynamic measurement techniques.

Stanford University presented their work on carrier transport and recombination parameters in heavily doped silicon. They presented data of minority carrier diffusivity in both p- and n-type heavily doped silicon covering a broad range of doping concentrations from 10^{15} to 10^{20} atoms per cm^3 . One of the highlights of their results showed that minority carrier diffusivities are higher by a factor of 2 in silicon compared to majority carrier diffusivities.

Professor R. Swanson, of Stanford University, described the construction of a 22.2% efficient single-crystal silicon solar cell fabricated at Stanford. The cell dimensions were 3×5 mm and 100 μm thick with a base lifetime of 500 μs . The cell featured light trapping between a texturized top surface and a reflective bottom surface, small point contact diffusions, alternating between n-type and p-type in a polka-dot pattern on the bottom surface, and a surface passivation on all surfaces between contact regions. A V_{oc} of 0.681 V, a J_{sc} of 41.5 mA/cm^2 , and a fill factor of 0.786 was reported for the 22.2% efficient cell.

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The University of Washington presented their work on investigating the passivation of silicon surfaces using SiN_x . They used high-frequency capacitance voltage (CV) measurements to determine the interface state density at midgap (D_{ss}). They indicated that the SiN_x/Si interface exhibits values of D_{ss} larger for n-type substrates than for p-type substrates and that, further, after heat treatment, this difference becomes even more pronounced. Also, it was found that the interface state density for $\text{SiN}_x/\text{p-type silicon}$ is essentially independent of dopant concentration, and the D_{ss} for $\text{SiN}_x/\text{n-type silicon}$ interface increases from 10^{12} to 10^{13} states $\text{cm}^{-2} \text{eV}^{-1}$ as the phosphorus concentration increases from 10^{16} to 10^{18} cm^{-3} . These results suggest that SiN_x can passivate a P^+/n cell more effectively than an n^+/p cell. The University of Washington also indicated that they are working on special structures that will allow measurement of both surface recombination velocity and interface state density.

Westinghouse described their work on achieving higher efficiency cells by directing efforts toward identifying carrier loss mechanisms, designing new cell structures, and developing new processing techniques. Their work, using techniques such as deep-level transient spectroscopy (DLTS), laser-beam-induced current (LBIC), and transmission electron microscopy (TEM), indicated that dislocations in web material rather than twin planes were primarily responsible for limiting diffusion lengths in web. They described their work in hydrogen implantation which indicated that they can improve lifetimes and cell efficiencies from 19 to 120 μm , and 8 to 10.3% (no AR), respectively, by implanting hydrogen at 1500 eV and a beam current density of 2.0 mA/cm^2 . Some of their processing improvements included use of a double-layer AR coating (ZnS and MgF_2) and an addition of an aluminum back surface reflector. Cells of more than 16% efficiency have been achieved.